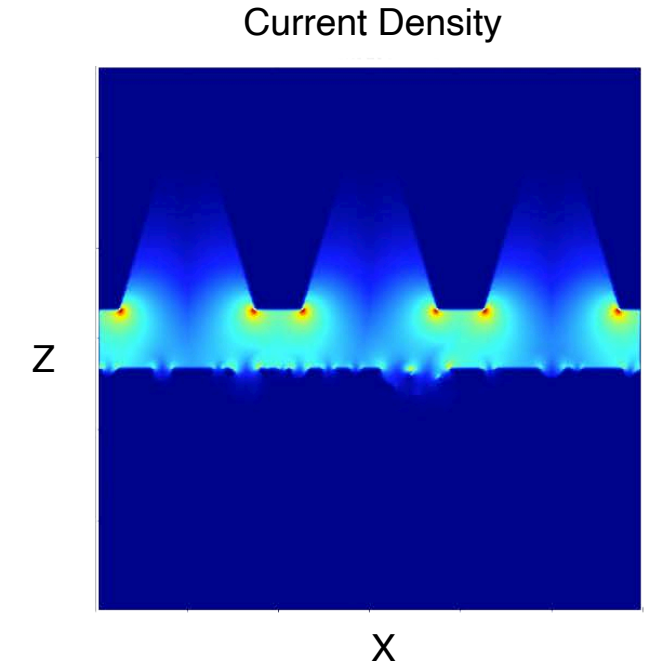
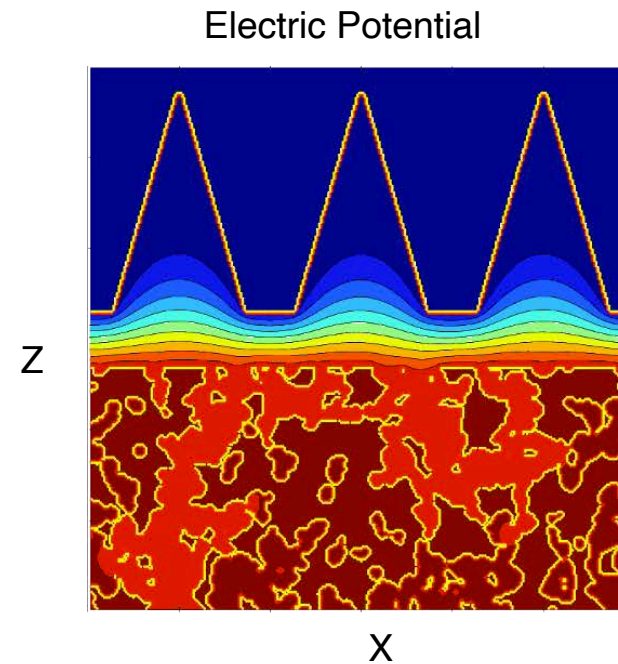
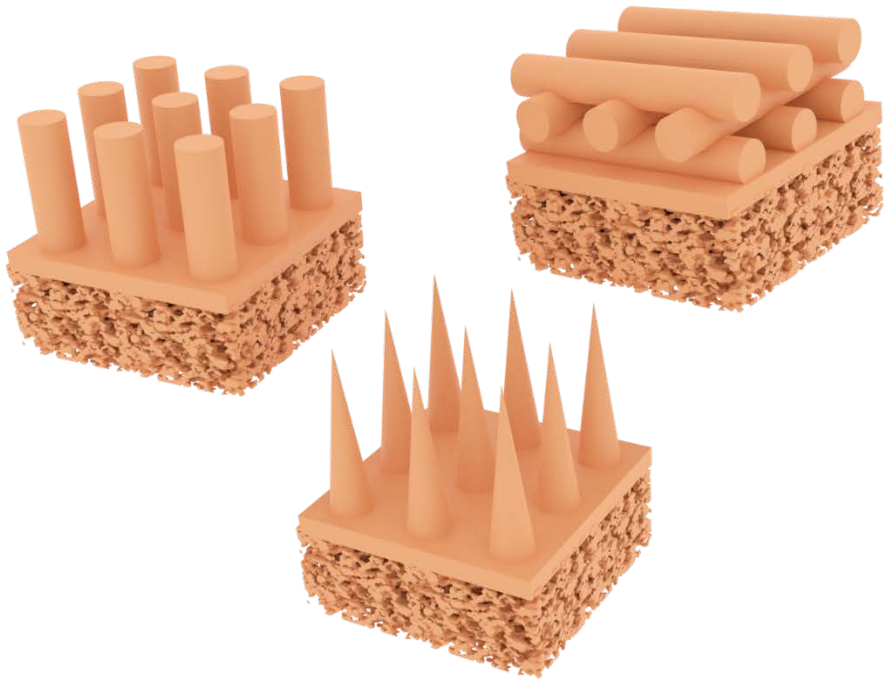


3D Printed, Low Tortuosity Garnet Framework For Beyond 500 Wh/kg Batteries

Eric D. Wachsman and Liangbing Hu



Overview

Timeline

- Project Start: 10/01/2017
- Project End: 03/31/2021
- Percent Complete:

Budget

- Total Project Funding: \$1,333,334
 - DOE Share: \$1,200,000
 - Cost Share: \$133,334
- FY 2020 Funding received: \$800,000

Barriers

- Garnet electrolytes provide high ionic conductivity and enable Li-metal anodes; however, are typically limited to planar low surface area electrode/electrolyte interfaces.
- Extending interfacial surface area in 3D enables thicker electrodes for higher energy density and potentially increases C-rate; however, solid-state battery transport models don't currently exist.
- 3D printed solid-state electrolytes enable fabrication of controlled architectures for determination of transport models and demonstration of higher energy density and C-rate solid-state batteries

Partners

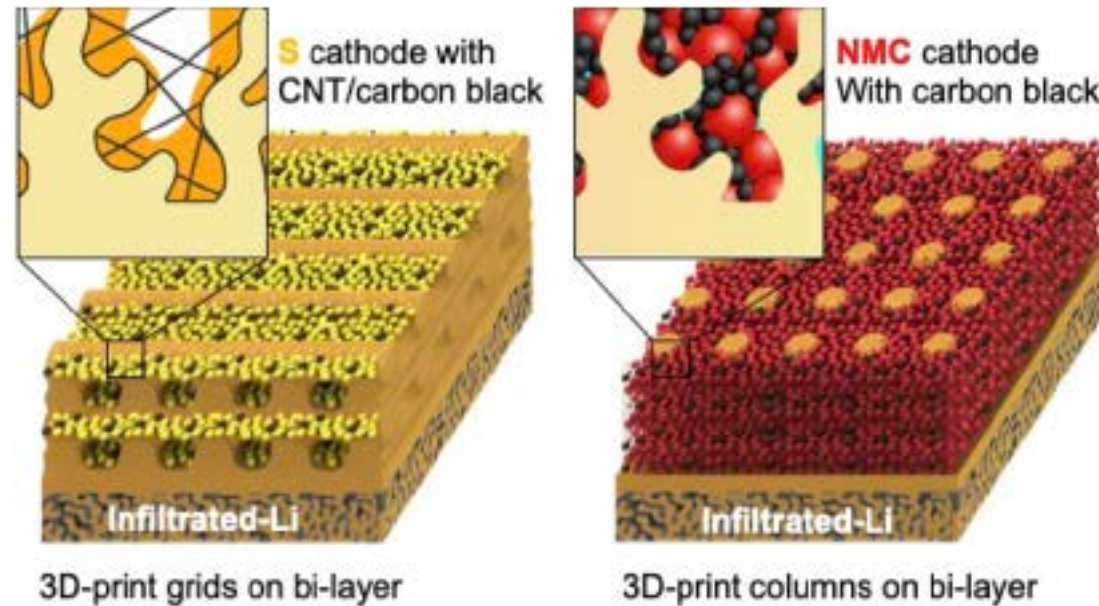
- Longstanding collaboration with Prof. Venkataraman Thangadurai



Relevance

Objectives

- Develop 3D ordered porous solid-state electrolyte structures that facilitate fast ion transport, enabling thicker electrodes for higher energy density, and higher C-rates for higher power density
- Demonstrate Li-S and Li-NMC batteries with ≥ 500 Wh/kg for ≥ 1000 cycles at a C/3 rate



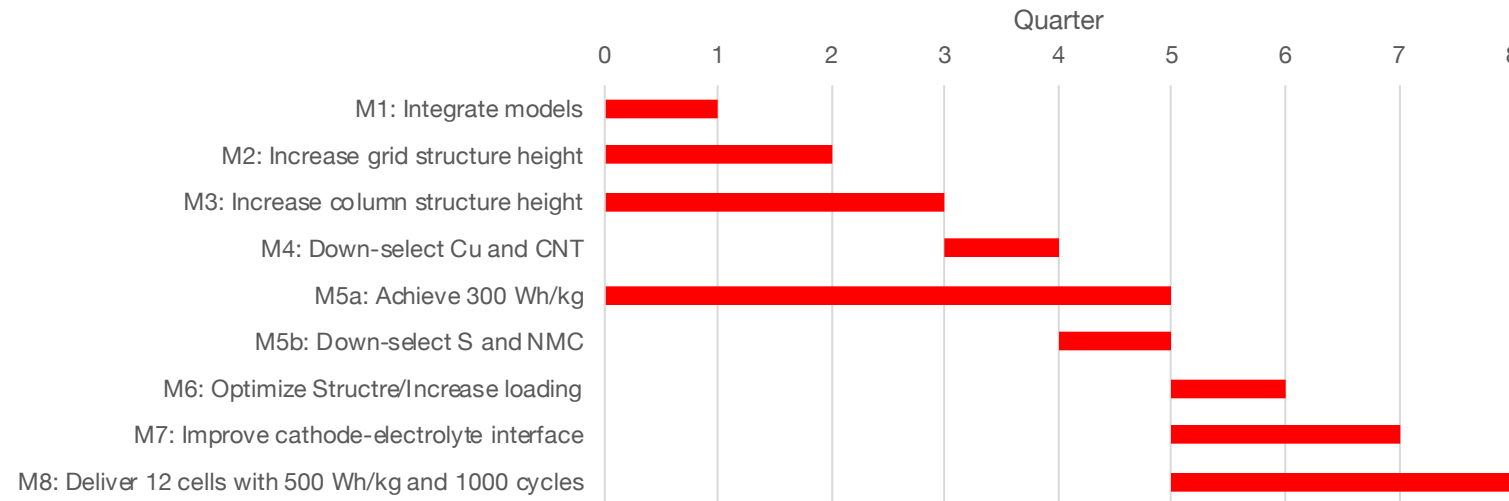
Impact

- Develop structure-property relationships in garnet electrolyte batteries to inform designs for improved performance
- Establish groundwork to help researchers develop batteries for high-demand applications

Approach and Milestones

Approach

- Develop solid-state ionic and electronic transport models to optimize the structure and experimentally validate models
- Develop 3D printing techniques and fabricate high porosity, low tortuosity $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ – garnet (LLZ) structures
- Fabricate and demonstrate high energy density 3D printed solid-state batteries



FY19Q1 Milestone: Integrate models to cathode structures (**Completed**)

FY19Q2 Milestone: Increase grid cathode structure height to achieve model design (**Completed**)

FY19Q3 Milestone: Increase column cathode structure height to achieve model design (**Completed**)

FY20Q4 Milestone: Down-select between Cu-porous and C-porous for Li metal anode (**Completed**)

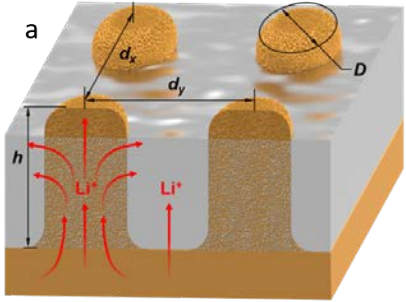
FY20Q5 Milestone: Achieve 300 Wh/kg and down-select between S and NMC cathodes (**In-progress**)

FY20Q6 Milestone: Optimize structure and increase active loading (**In-progress**)

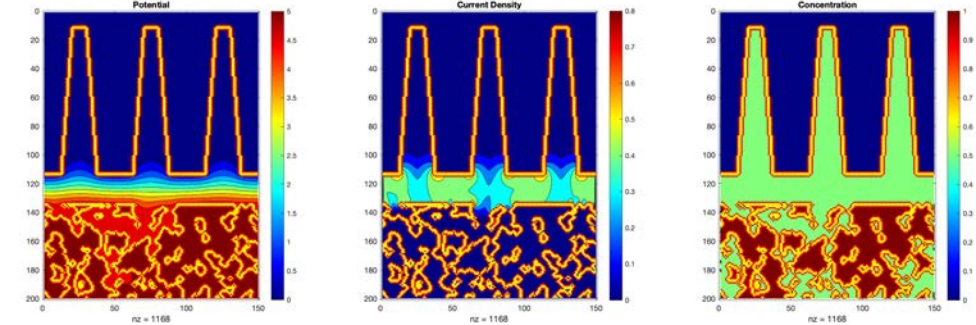
FY20Q7 Milestone: Improve cathode-electrolyte interface to achieve >200 cycles with 500 Wh/kg

FY21Q8 Milestone: Deliver 12 cells with an energy density >500 Wh/kg and 1000 cycles

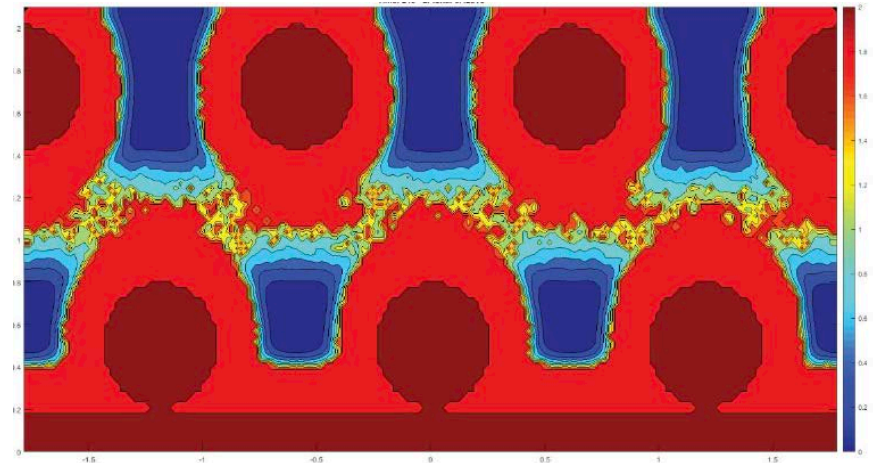
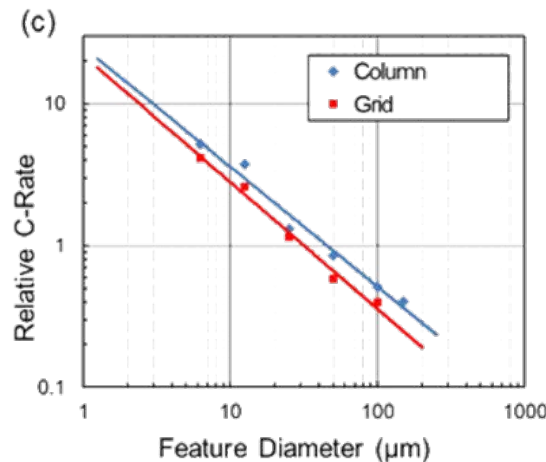
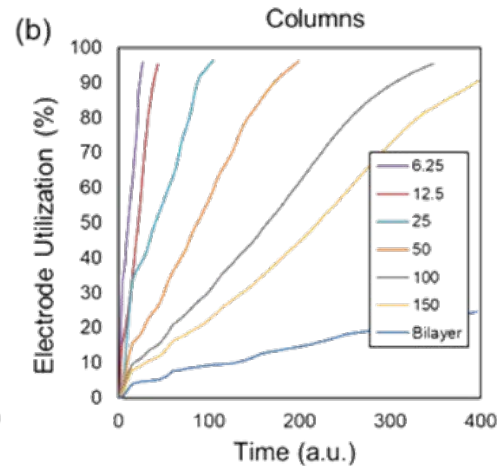
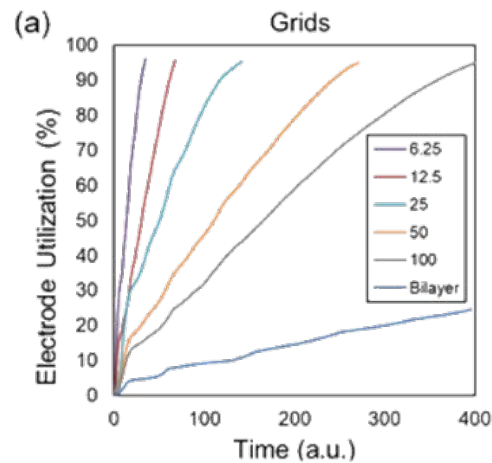
Modeling Solid-State Ionic Transport in 3D Structures



- Developed transport models to predict the utilization of intercalation cathodes such as NMC.
- Current work to model the transport of multiple chemical species in more complex conversion cathodes such as Sulfur



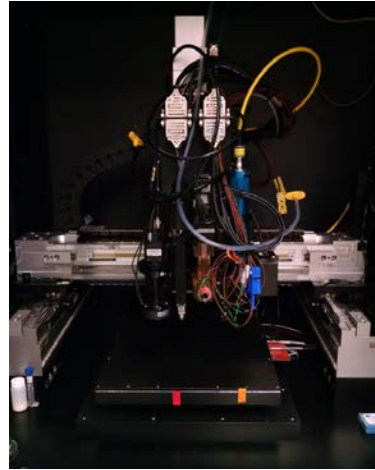
- Model can be applied to any 3D framework – including grid, column, and random porous structures
- Simulations show that finer features with low tortuosity lead to optimal cathode utilization and energy density



- Staggering layers leads to higher energy density by decreasing the longest diffusion distances

FY19Q1 Milestone: Integrate models to cathode structures (Completed)

Fabricate 3D High Porosity, Low Tortuosity, LLZ Structures



- Developed ink compositions to optimize rheology, as well as drying and sintering conditions to 3D print multiple low-tortuosity LLZ structures

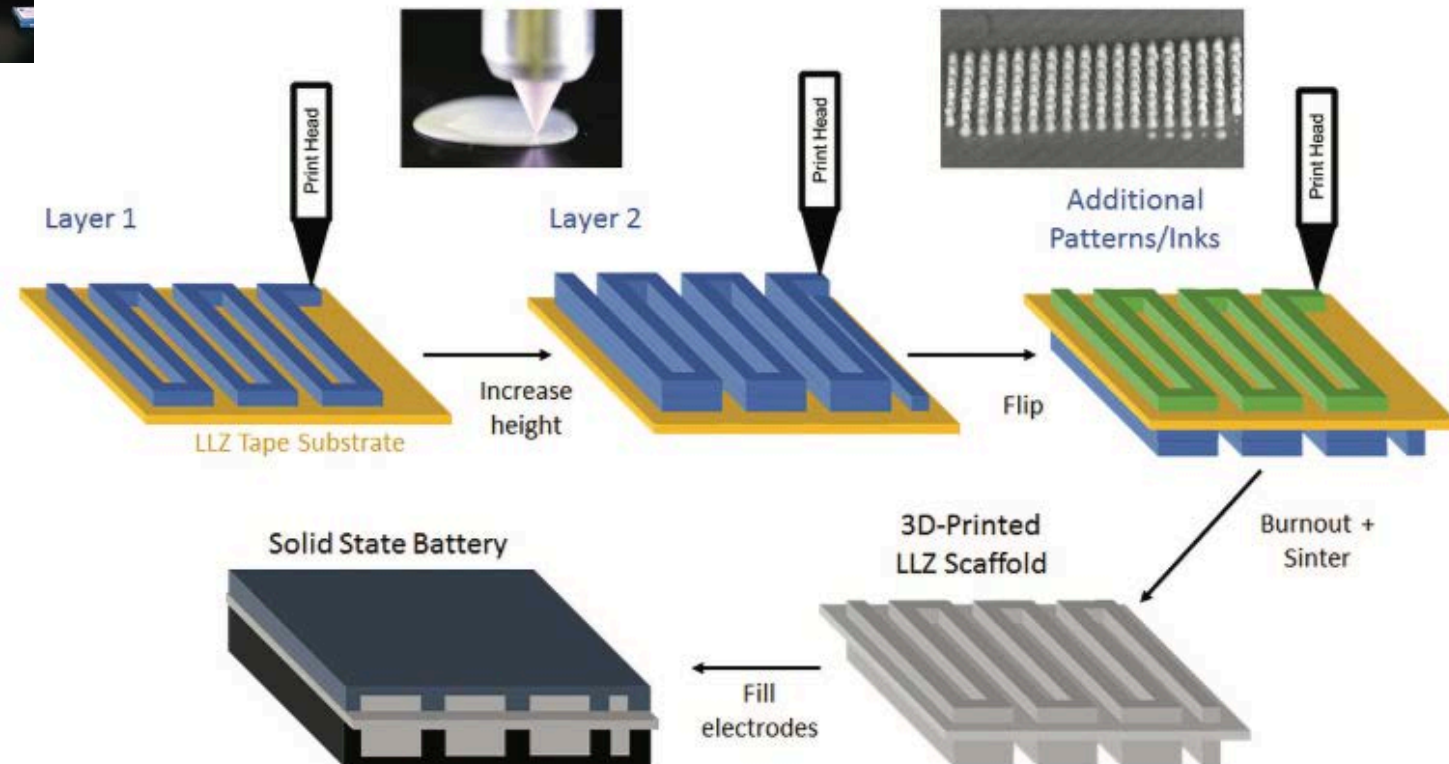
COMMUNICATION

Solid Electrolytes

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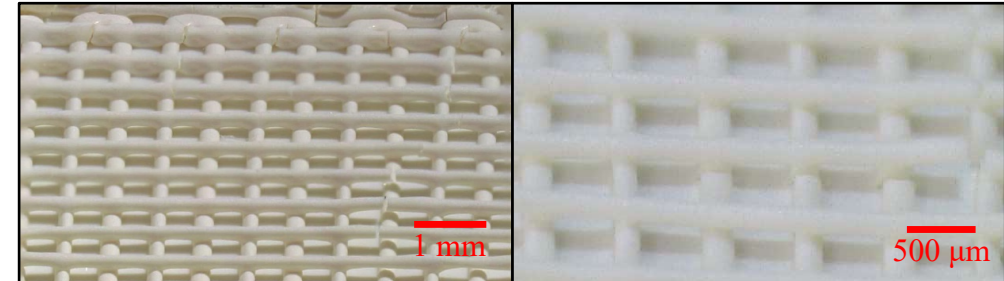
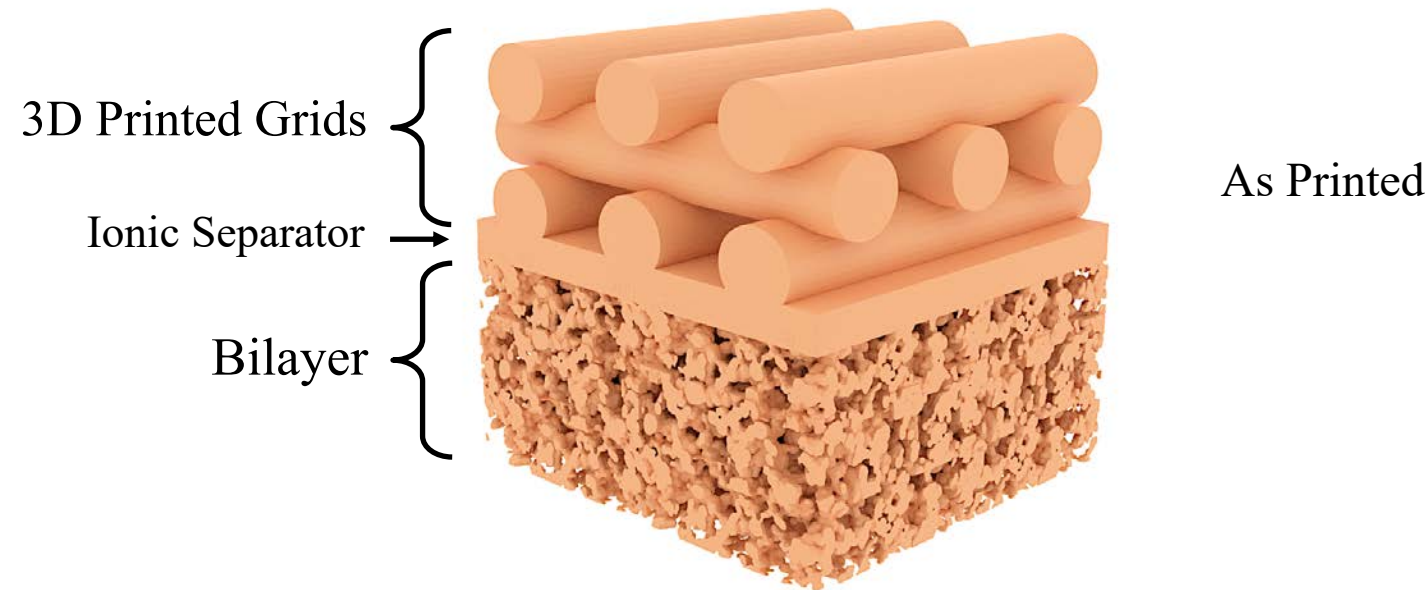
3D-Printing Electrolytes for Solid-State Batteries

Dennis W. McOwen, Shaomao Xu, Yunhui Gong, Yang Wen, Griffin L. Godbey, Jack E. Gritton, Tanner R. Hamann, Jiaqi Dai, Gregory T. Hitz, Liangbing Hu,* and Eric D. Wachsman*



Fabricate 3D High Porosity, Low Tortuosity, LLZ Structures

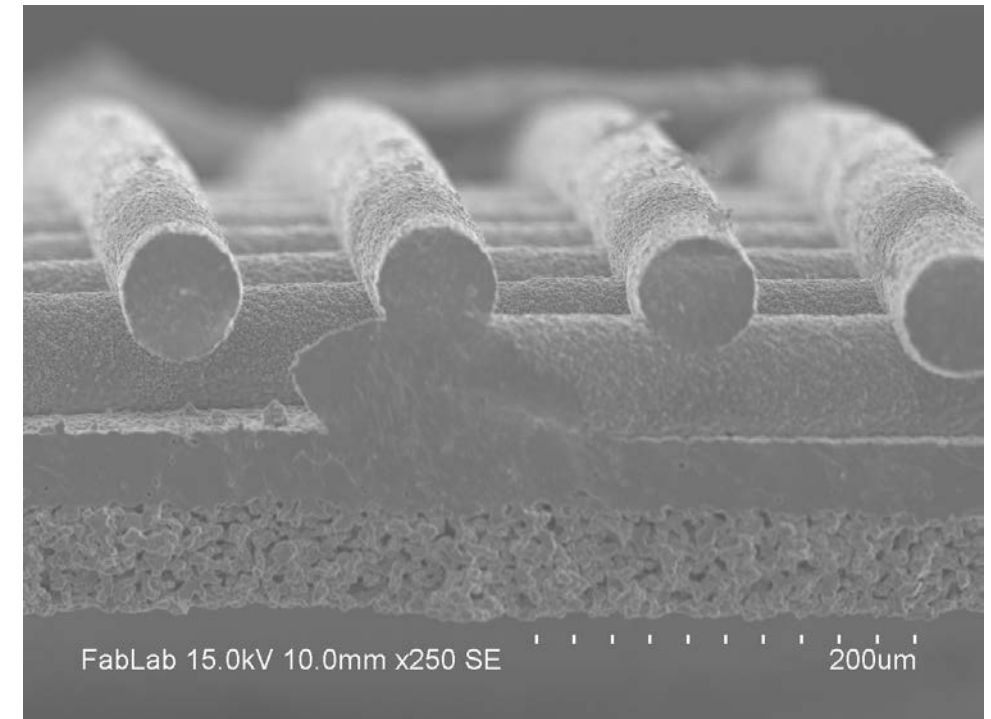
- Grid structure has better mechanical strength than columns and can infiltrate sulfur cathodes



- Achieved sintered $\sim 100\ \mu\text{m}$ LLZ grid height on bilayer garnet structure

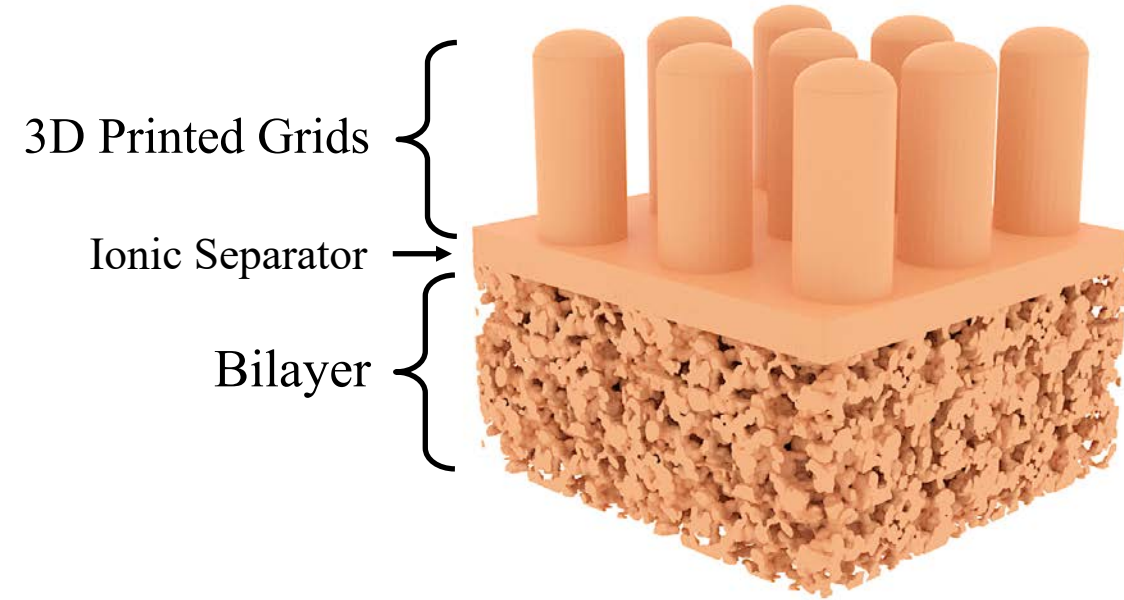
FY19Q2 Milestone: Increase grid cathode structure height to achieve model design (**Completed**)

Sintered

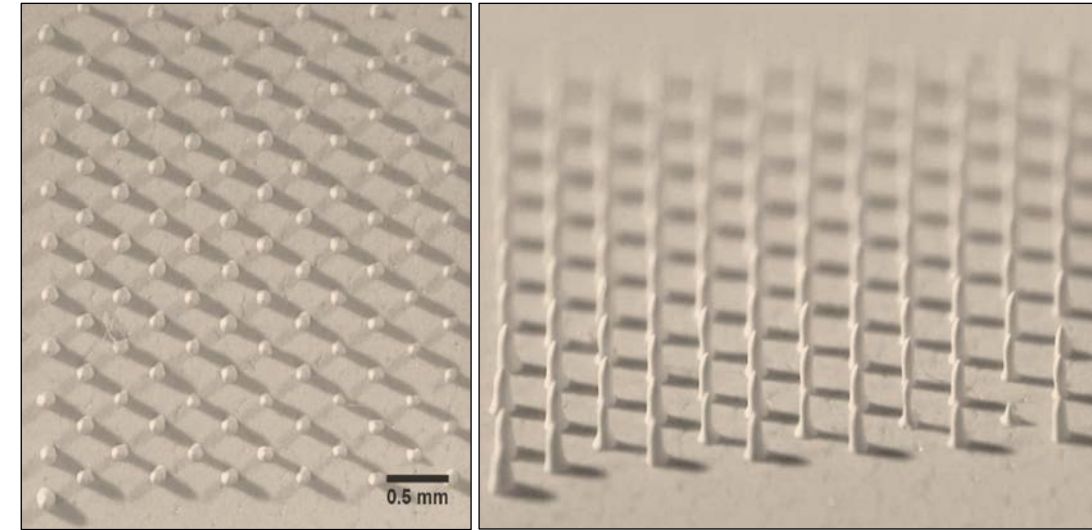


Fabricate 3D High Porosity, Low Tortuosity, LLZ Structures

- Columns are easier to fill with cathode material such as NMC because of low tortuosity

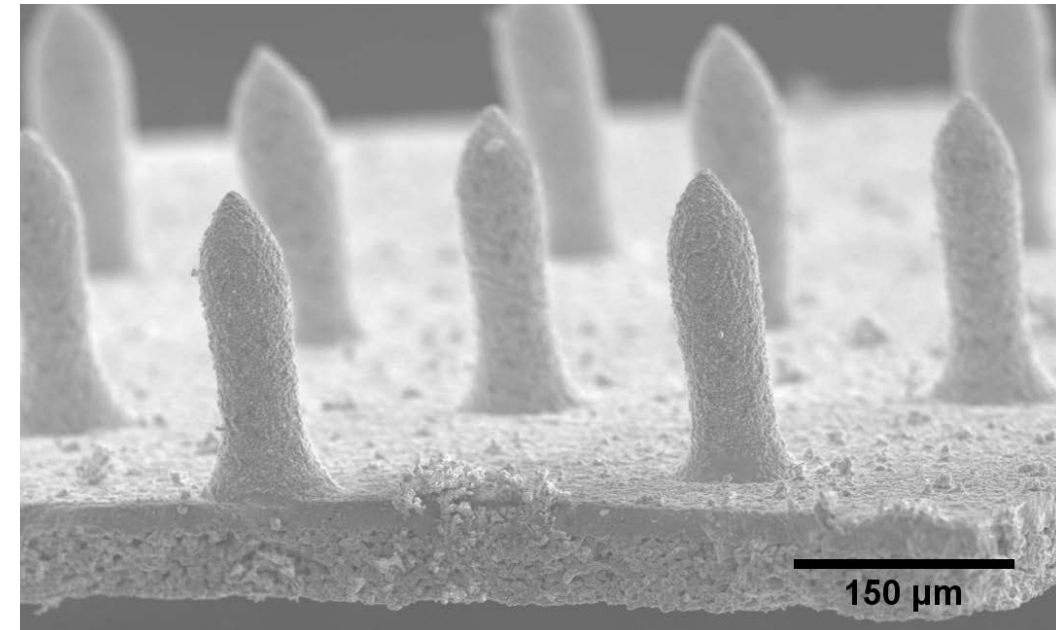


As Printed



- Achieved sintered $\sim 200\ \mu\text{m}$ LLZ column height on bilayer garnet structure

Sintered

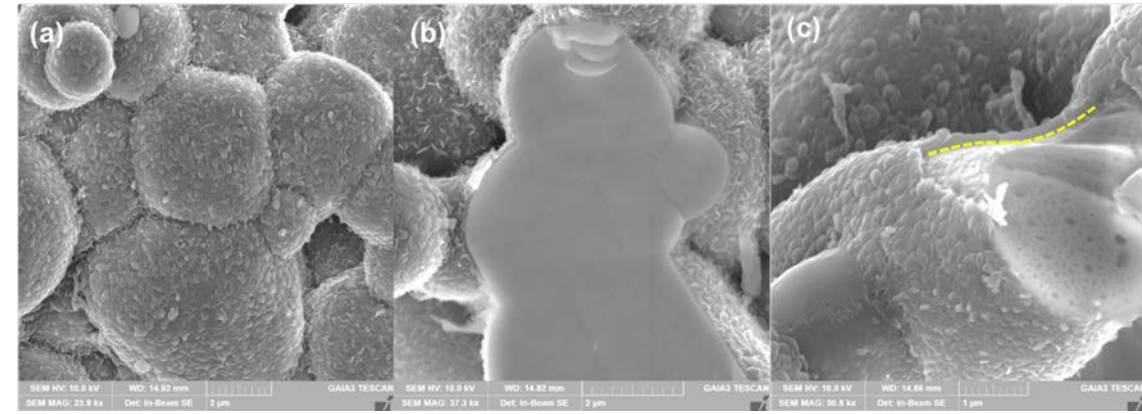
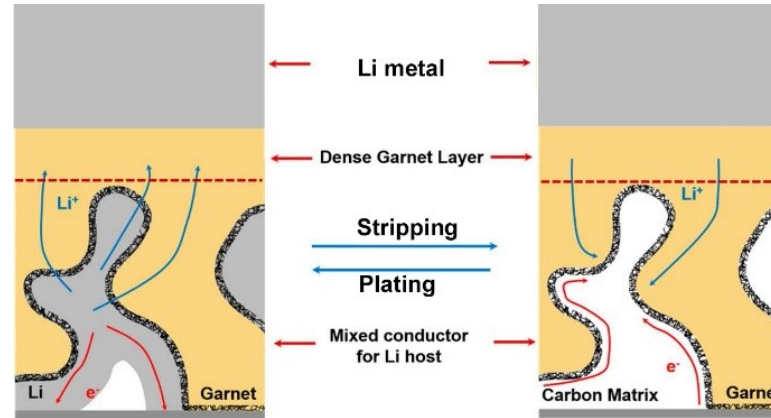


FY19Q3 Milestone: Increase column cathode structure height to achieve model design (**Completed**)

Develop “Li-Free” Solid-State Anodes and Down Select

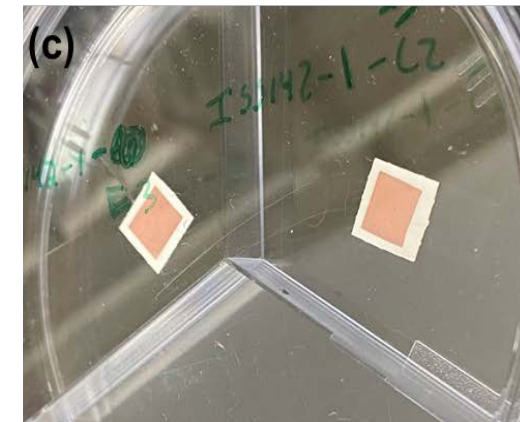
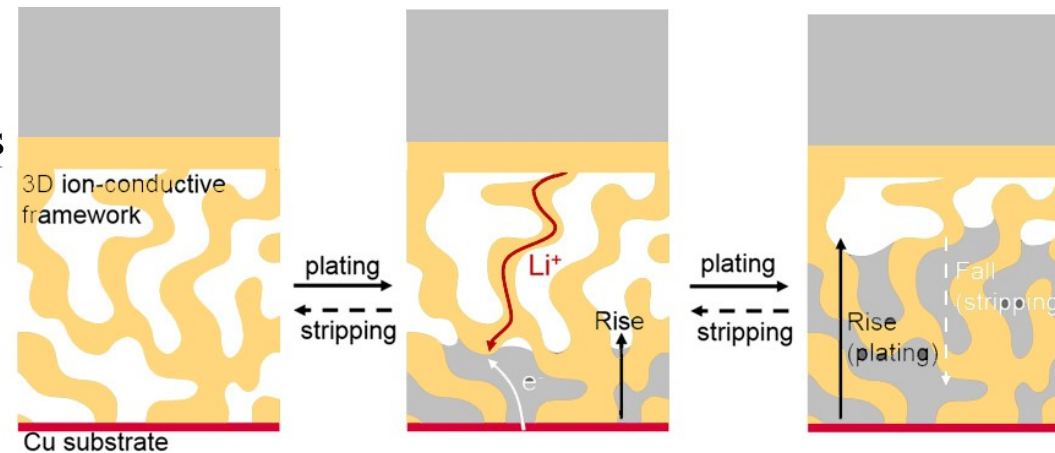
- “Li-Free” anodes reduce cell mass and cost, and simplify processing for Li-metal anodes

- Conformal coating of CNT inside garnet pores creates mixed electron-ion conducting framework to enable “Li-Free” anodes



Conformal CNT layer inside LLZ pores

- Sputtered Cu layer on the exterior surface of the porous LLZ layer provides electrical contact for Li deposition and Li rises towards the dense layer during plating

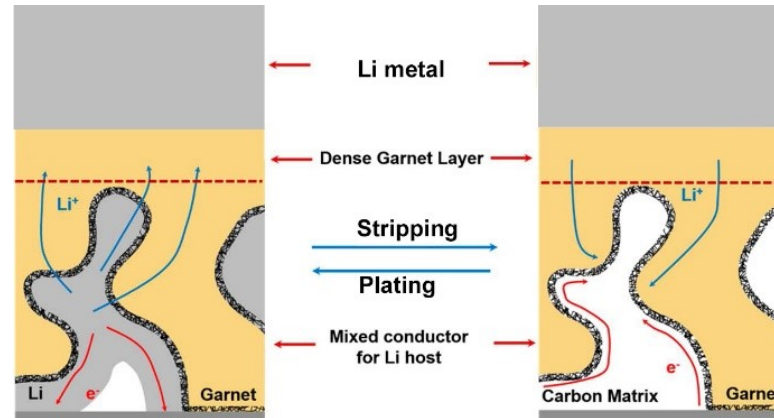


Sputtered Cu layer on LLZ surface

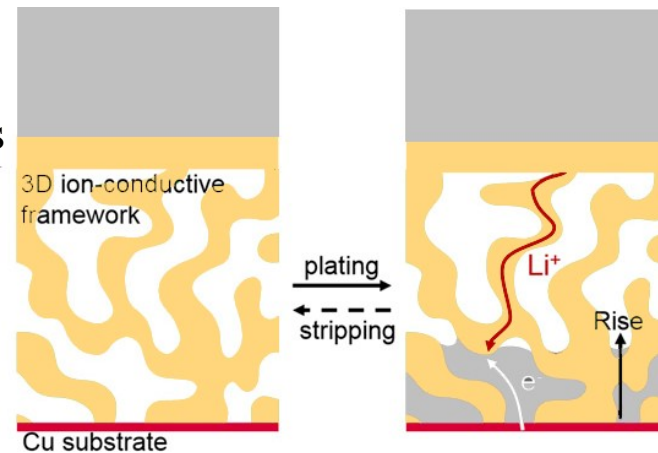
Develop “Li-Free” Solid-State Anodes and Down Select

- “Li-Free” anodes reduce cell mass and cost, and simplify processing for Li-metal anodes

- Conformal coating of CNT inside garnet pores creates mixed electron-ion conducting framework to enable “Li-Free” anodes

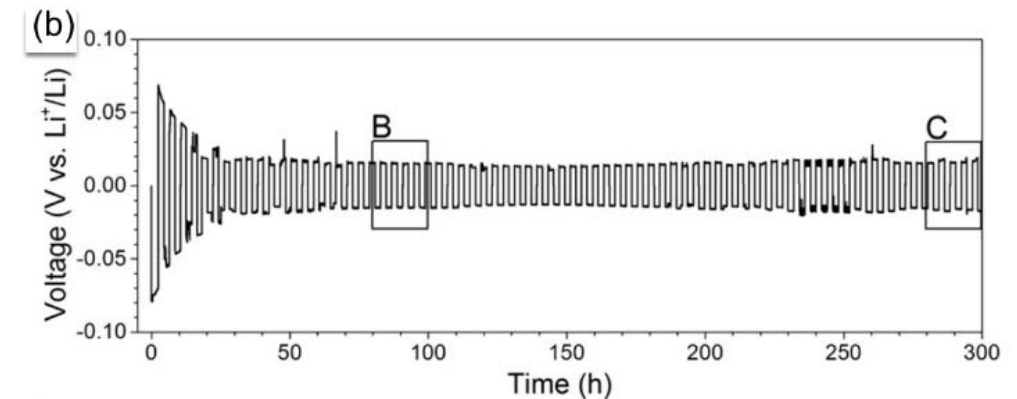
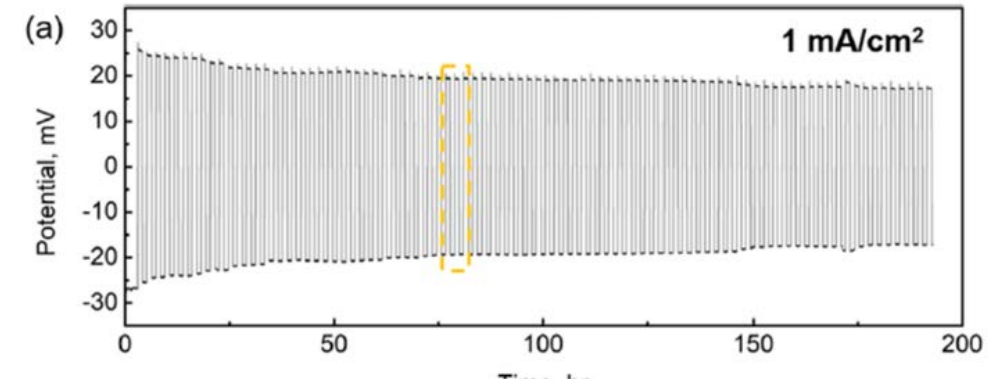


- Sputtered Cu layer on the exterior surface of the porous LLZ layer provides electrical contact for Li deposition and Li rises towards the dense layer during plating



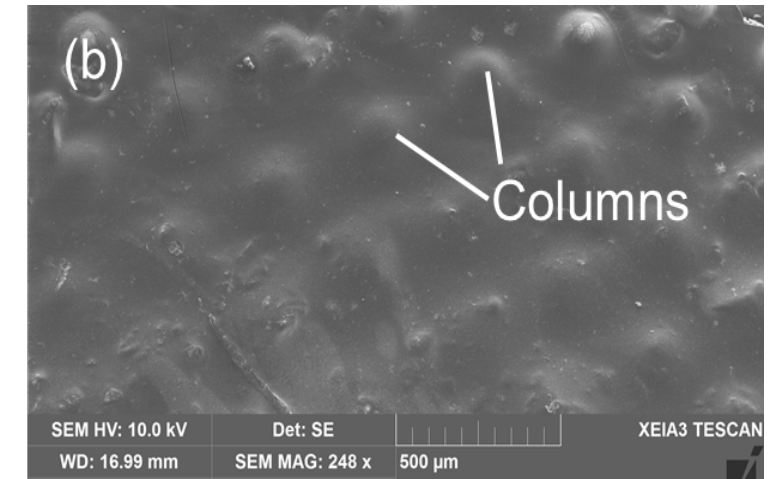
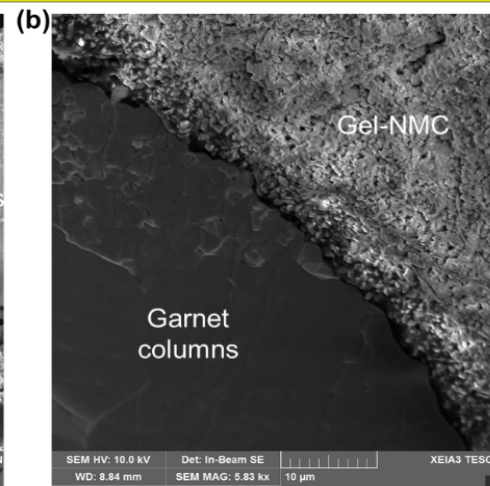
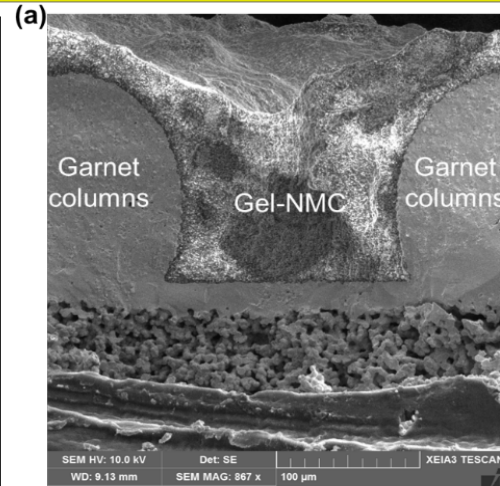
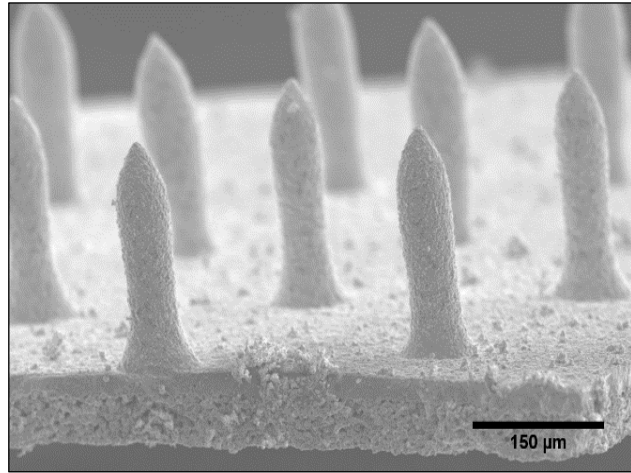
CNT properties preferred for “Li-Free” anodes

Cycling of cell with CNT current collector at 1 mA/cm²
(Ref.: Nano Lett. 2018, 18, 3926-3933)

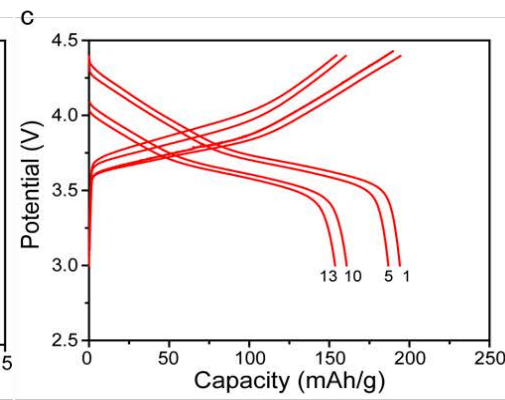
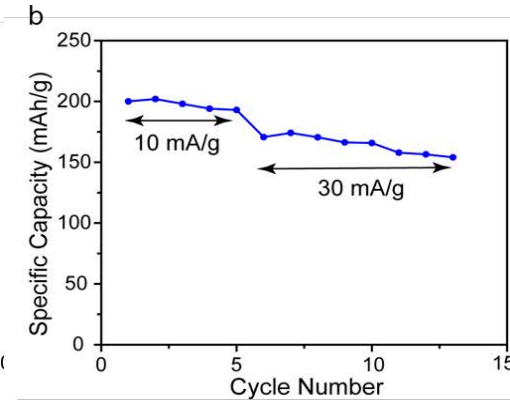
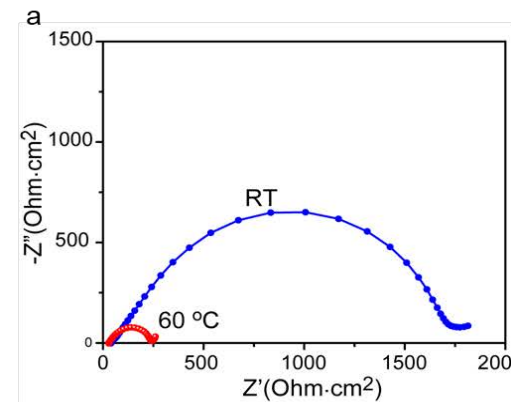


Cycling of cell with Cu current collector at 0.5 mA/cm²
(Ref.: PNAS, 2018, 115, 3770-3775)

Fabricate and Demonstrate Full Cells with 3D Printed LLZ Cathode



- NMC filled column structures
- Electrochemical performance of initial Li-NMC cell at 60° C with NMC mass loading of $\sim 14 \text{ mg/cm}^2$ and current density of 10-30 mA/g. (a) EIS of full cell at room temperature (blue) and 60° C (red). (b) Discharge capacity vs cycle number. (c) Voltage profiles of cycles 1 and 5 (10 mA/g) and cycles 10 and 13 (30 mA/g).



Response to Previous Year Comments

- Not reviewed last year

Remaining Challenges and Upcoming Work

- Demonstrate energy (300 Wh/kg) density for Li-S or Li-NMC cells with stable cycling
- Optimize 3D structures to improve loading
- Improve cathode-electrolyte interface to achieve >200 cycles with 500 Wh/kg
- Demonstrate high energy (500 Wh/kg) density for Li-S or Li-NMC cells with over 1000 cycles

Proposed Future Research

FY20

- Demonstrate energy (300 Wh/kg) density for Li-S or Li-NMC cells with stable cycling
- Optimize 3D structures to improve loading
- Improve cathode-electrolyte interface to achieve >200 cycles with 500 Wh/kg



Summary

FY19

- Developed models capable of designing 3D geometry structures (grid, column, porous, etc.)
- Models showed finer 3D features will more optimally utilize cathode active materials
- 3D printing ink properties determined

FY20

- Achieved high aspect ratio column structures, $\sim 200\text{ }\mu\text{m}$ tall
- Achieved tall ($\sim 100\mu\text{m}$) grid structures with $50\text{ }\mu\text{m}$ diameters and a separation of $150\text{ }\mu\text{m}$
- Down selected “Li Free” anode structure to CNT coated pores vs external Cu current collectors
- Initiated 3D printed LLZ full cell fabrication and testing
- Achieve 300 Wh/kg and down-select between S and NMC cathodes
- Optimize structure and increase active loading
- Improve cathode-electrolyte interface to achieve >200 cycles with 500 Wh/kg

- **FY21**

- Deliver 12 cells with an energy density $>500\text{ Wh/kg}$ and 1000 cycles

